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(54) Title: LUBRICATING OIL COMPOSITION

(57) Abstract: A lubricating oil composition comprising a β beta-dithiophosphorylpropionic acid (a), a polyalkylenepolyamide (B) and base oil.

LUBRICATING OIL COMPOSITION

The present invention relates to a lubricating oil composition which has excellent extreme pressure performance, and which has excellent anti-rust properties in severe operating environments.

5 The wear surfaces of equipment are being subjected to ever more severe conditions as a result of increased running speeds, increased loads and increases in efficiency which have arisen in recent times, and scorching of the wear surfaces is likely to occur as a
10 result of the breakdown of the lubricating oil film.

Consequently, extreme pressure additives which react with the metal surface and maintain the lubricating properties at the wear surface are added in suitable amounts to the lubricating oils which are used under such
15 severe conditions in order to prevent sticking of the wear surfaces. However, anti-rust agents are used in lubricating oils not in relation to the lubrication performance but to protect the machine parts from rusting when water or seawater is admixed. It is known in
20 general that anti-rust agents are strongly adsorbed on metal surfaces and generally form an anti-rust film on the metal surface and so prevent direct contact between the metal and water from occurring and the resultant formation of rust. However, reaction between the metal
25 surface and an extreme pressure additive at the wear surface is also impeded and the effect of the extreme pressure additive is to a large extent lost as a result.

It is therefore desirable to provide ashless lubricating oil compositions containing no metal and which, from the viewpoints of the lubrication performance and the anti-rust performance of the lubricating oil, not
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- 2 -

only maintain excellent extreme pressure performance even under severe lubrication conditions, but which also have excellent anti-rust properties.

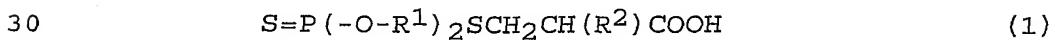
It has been surprisingly found in the present
5 invention that the problem of the effective weakening of the properties of extreme pressure additives by anti-rust agents also present in a lubricating oil composition can be solved by combining specific extreme pressure additives and specific anti-rust agents in such
10 lubricating oil compositions.

The present invention provides lubricating oil compositions comprising β -dithiophosphoryl propionic acids and specific anti-rust additives with which there is virtually no loss of the load resistance capacity of
15 the β -dithiophosphorylpropionic acids therein due to the presence of said anti-rust additives.

β -dithiophosphorylpropionic acids are excellent extreme pressure additives which improve the capacity of gear wheels, as described in Japanese Unexamined Patent
20 Application Laid Open H10-67993. However, this load resistance capacity can be greatly reduced depending on the type of anti-rust additive with which they are combined.

The present invention provides a lubricating oil
25 composition comprising a β -dithiophosphorylpropionic acid (A), a polyalkylenepolyamide (B) and base oil.

In a preferred embodiment, β -dithiophosphoryl-propionic acid (A) is represented by general formula (1) below:



wherein R^1 , which may be identical or different, represents a branched alkyl group of from 3 to 8 carbon

- 3 -

atoms, and R² represents a hydrogen atom or a linear or branched alkyl group of from 1 to 4 carbon atoms.

The branched alkyl group, R¹, can be chosen from the following groups:- isopropyl group, the branched butyl groups, the branched pentyl groups, the branched hexyl groups, the branched heptyl groups and the branched octyl groups.

Furthermore, examples of R² include hydrogen, and the methyl group, the ethyl group, the propyl groups and the butyl groups. It is particularly preferred that R² is hydrogen or a methyl.

Specific examples of such compounds include 3-(O,O-diisopropylidithiophosphoryl)propionic acid, 3-(O,O-diisopropylidithiophosphoryl)-2-methylpropionic acid, 3-(O,O-diisobutyldithiophosphoryl)propionic acid and 3-(O,O-diisobutyldithiophosphoryl)-2-methylpropionic acid.

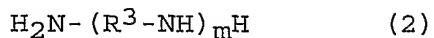
The amount of the β -dithiophosphorylpropionic acid (A) used in the lubricating oil composition of the present invention is preferably from 0.001 to 0.5 part by weight, more preferably from 0.005 to 0.2 part by weight, and most preferably from 0.01 to 0.1 part by weight, per 100 parts by weight of base oil.

If the amount of the β -dithiophosphorylpropionic acid (A) added is less than 0.001 part by weight then a satisfactory synergistic effect may not be obtained, whereas if the amount of (A) added exceeds 0.5 part by weight, the lubrication performance reaches saturation and the thermal oxidation stability, the hydrolysis stability and the corrosion properties may be adversely affected.

In a preferred embodiment, the polyalkylenepolyamide (B) is obtained by reacting,

- 4 -

(i) a polyalkylenepolyamine represented by the general formula (2) below:-



wherein R^3 represents an alkylene group of from 2 to 4 carbon atoms, and m is an integer of value from 2 to 6, with

(ii) at least one type of carboxylic acid selected from the group comprising saturated monocarboxylic acids having from 12 to 30 carbon atoms and unsaturated 10 monocarboxylic acids having from 18 to 24 carbon atoms.

The aforementioned carboxylic acid is preferably a mixture of aliphatic monocarboxylic acids, and this mixture is conveniently selected from among the group comprising mixtures of aliphatic monocarboxylic acids of which the aliphatic group is a linear chain saturated alkyl group which has from 12 to 30 carbon atoms and aliphatic monocarboxylic acids of which the aliphatic group is a branched saturated alkyl group which has from 12 to 30 carbon atoms, and mixtures of aliphatic 15 monocarboxylic acids of which the aliphatic group is a linear chain unsaturated alkyl group which has from 18 to 24 carbon atoms and aliphatic monocarboxylic acids of which the aliphatic group is a branched saturated alkyl group which has from 12 to 30 carbon atoms. 20

Actual examples of the aforementioned polyalkylenepolyamines of (i) above, which can be represented by the general formula (2) and which can be used in the present invention, include 25 diethylenetriamine, triethylenetetramine, tetraethylenepentamine, pentaethylenehexamine, hexaethyleneheptamine, tetrapropylenepentamine and hexabutyleneheptamine.

Unsaturated fatty acids alone, linear chain saturated fatty acids alone, branched saturated fatty

- 5 -

acids alone, or mixtures of unsaturated fatty acids and linear chain saturated fatty acids, mixtures of unsaturated fatty acids and branched saturated fatty acids or mixtures of branched saturated fatty acids and linear chain saturated fatty acids, can be used for the aforementioned monocarboxylic acid of (ii) above which is reacted with the aforementioned polyalkylenopolyamine of (i).

The unsaturated fatty acids are monocarboxylic acids which have from 18 to 24 carbon atoms, and which may have a hydroxyl group. Typical examples thereof include oleic acid, elaidic acid, erucic acid, brassidic acid, linolic acid, linoleic acid, recinolic acid and arachidonic acid.

The branched saturated fatty acids are monocarboxylic acids which have from 12 to 30 carbon atoms. Typical examples thereof include 2-methylheptadecanoic acid, 16-methylheptadecanoic acid, 2-octadecanoic acid, 2-methyl-octadecanoic acid, 10-methyloctadecanoic acid, 15-ethylheptadecanoic acid, 3-methylnonadecanoic acid, 2-butyl-2-heptylnonanoic acid, 2-ethyleicosanoic acid, 20-methyleneicosanoic acid, 3-methyltricosanoic acid, 10-methyltetrcasanoic acid, 18-methyltetracosanoic acid, 13,16-dimethyltricosanoic acid, 3,13,19-trimethyltricosanoic acid and isostearic acid.

The linear chain saturated fatty acids are monocarboxylic acids which have from 12 to 30 carbon atoms, which may have hydroxyl groups. Typical examples thereof include lauric acid, myristic acid, palmitic acid, stearic acid, 12-hydroxystearic acid, arachic acid, behenic acid, lignoceric acid, cerotic acid, montanic acid and melissic acid.

The aforementioned aliphatic monocarboxylic acid component is centred around the aliphatic monocarboxylic acids in which the aliphatic group is a linear chain saturated or unsaturated carboxylic acid, but with these

- 6 -

alone there are cases where a group which provides solubility in oil is lacking and so the solubility is preferably adjusted with the conjoint use of some aliphatic monocarboxylic acid which has a branched alkyl group.

The preferred combinations are (a) combinations of aliphatic monocarboxylic acids which have a linear chain saturated alkyl group and aliphatic monocarboxylic acids which have a branched saturated alkyl group (for example, mixtures of stearic acid and isostearic acid) and (b) combinations of aliphatic monocarboxylic acids which have a linear chain unsaturated alkyl group and aliphatic monocarboxylic acids which have a branched saturated alkyl group.

The proportions of the linear chain type aliphatic monocarboxylic acid and branched type aliphatic monocarboxylic acid in these combinations may vary according to the nature of the base oil which is being used, but they are generally used in proportions within the range of from 10 to 100 mol% of the linear chain type aliphatic monocarboxylic acid and of from 90 to 0 mol% of branched type aliphatic monocarboxylic acid.

The reaction of the aforementioned polyalkylenepolyamine of (i) and the aforementioned monocarboxylic acid of (ii) can conveniently be carried out for from 2 to 3 hours at a temperature of from 200 to 220°C in general to obtain the prescribed amide. The amount of monocarboxylic acid used at this time is preferably not more than $(m+1)$ mol per 1 mol of the polyalkylenepolyamide in order that from 50 to 90% of the $(m+1)$ amino groups are converted to amide.

The amount of polyalkylenepolyamide (B) used in the lubricating oil composition of the present invention is preferably from 0.005 to 1 part by weight, more

- 7 -

preferably from 0.01 to 0.5 part by weight, and most preferably from 0.02 to 0.5 part by weight, per 100 parts by weight of base oil.

5 If the amount of (B) added is less than 0.005 part by weight, then the anti-rust performance is inadequate, whereas if more than 1 part by weight of (B) is added the anti-rust performance reaches saturation and there may be a pronounced adverse effect on the extreme pressure performance and resistance to emulsion formation.

10 The base oil comprised in the lubricating oil composition of the present invention is not subject to any particular limitation. Preferably, said base oil comprises petroleum-based oil and/or synthetic hydrocarbon-based oil.

15 Preferred base oils are those which have:

a kinematic viscosity of from 2 to 680 mm²/s (40°C), more preferably of from 5 to 320 mm²/s (40°C), and most preferably of from 8 to 220 mm²/s (40°C);

20 a total sulphur content (wt%) of from 0 to 1%, and preferably of from 0 to 0.3%;

a total nitrogen content (wt. ppm) of from 0 to 100 ppm, and more preferably of from 0 to 30 ppm; and/or

an aniline point of from 80 to 130°C, and more preferably of from 100 to 125°C.

25 The petroleum-based base oils which can be used in the present invention may be, for example, individual solvent refined base oils, hydrogenation refined base oils or highly hydrogenated and cracked base oils, or mixtures of such oils. Highly hydrogenated cracked base oils are base oils which have a viscosity index of at least 130 (typically from 145 to 155) obtained with a slack wax which has been cracked and solvent de-waxed as the raw material by isomerizing the linear chain paraffins to branched paraffins by hydrogenation cracking

- 8 -

in the presence of a catalyst (contact cracking), or base oils which have a viscosity index of at least 130 (typically from 145 to 155) obtained using heavy linear chain paraffins which have been obtained by Fischer-Tropsch polymerization using the carbon monoxide and hydrogen obtained by a gasification process (partial oxidation) of a natural gas (such as methane) and subjecting this to catalytic cracking and isomerization in the same way as above.

10 Furthermore, the synthetic hydrocarbon-based base oils which may be used in the present invention include the olefin oligomers obtained by the homopolymerization or copolymerization of monomers which have been selected from among the linear chain and branched olefinic 15 hydrocarbons which have from 3 to 15 carbon atoms, and preferably from 4 to 12 carbon atoms.

In the present invention, the petroleum-based base oils and synthetic hydrocarbon-based base oils can be used individually or in the form of mixtures.

20 In addition to the aforementioned components (A) and (B), suitable amounts of supplementary additives of the various types which are generally used can be added to the lubricating oil composition of the present invention, as required, in order to further improve the performance 25 thereof.

Supplementary additives that may be added to the lubricating oil composition of the present invention include lubricating oil additives such as antioxidants, 30 anti-rust agents, metal deactivators, cleaning and dispersing agents, anti-wear agents, extreme pressure additives, friction controlling agents, flow-point reducing agents, viscosity index increasing agents, anti-emulsification agents and anti-foaming agents.

Examples of amine-based antioxidants include 35 dialkyldiphenylamines such as p,p'-dioctyldiphenylamine

- 9 -

(manufactured by the Seiko Kagaku Co. under the trade designation "Nonflex OD-3"), p,p'-di- α -methylbenzyl-diphenylamine and N-p-butylphenyl-N-p'-octylphenylamine; monoalkyldiphenylamines such as mono-t-butylidiphenyl-amine and mono-octylidiphenylamine; bis(dialkylphenyl)-amines such as di(2,4-diethylphenyl)amine and di(2-ethyl-4-nonylphenyl)amine; alkylphenyl-1-naphthylamines such as octylphenyl-1-naphthylamine and N-t-dodecylphenyl-1-naphthylamine; arylnaphthylamines such as 1-naphthylamine, phenyl-1-naphthylamine, phenyl-2-naphthylamine, N-hexylphenyl-2-naphthylamine and N-octylphenyl-2-naphthylamine, phenylenediamines such as N,N'-diisopropyl-p-phenylenediamine and N,N'-diphenyl-p-phenylenediamine, and phenothiazines such as phenothiazine (manufactured by the Hodogaya Kagaku Co.: Phenothiazine) and 3,7-dioctylphenothiazine.

Examples of sulphur based antioxidants include dialkylsulphides such as didodecylsulphide, and dioctadecylsulphide; thiodipropionic acid esters such as didodecyl thiodipropionate, dioctadecyl thiodipropionate, dimyristyl thiodipropionate and dodecyloctadecyl thiodipropionate, and 2-mercaptopbenzimidazole.

Examples of phenol-based antioxidants include 2-t-butylphenol, 2-t-butyl-4-methylphenol, 2-t-butyl-5-methylphenol, 2,4-di-t-butylphenol, 2,4-dimethyl-6-t-butylphenol, 2-t-butyl-4-methoxyphenol, 3-t-butyl-4-methoxyphenol, 2,5-di-t-butylhydroquinone (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage DBH"), 2,6-di-t-butylphenol and 2,6-di-t-butyl-4-alkylphenols such as 2,6-di-t-butyl-4-methylphenol and 2,6-di-t-butyl-4-ethylphenol; 2,6-di-t-butyl-4-alkoxyphenols such as 2,6-di-t-butyl-4-methoxyphenol and 2,6-di-t-butyl-4-ethoxyphenol, 3,5-di-t-butyl-4-hydroxybenzylmercaptooctyl acetate, alkyl-3-(3,5-di-t-

- 10 -

butyl-4-hydroxyphenyl)propionates such as n-octyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Yonox SS"), n-dodecyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate and 2'-ethylhexyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate; 2,6-di-t-butyl- α -dimethylamino-p-cresol, 2,2'-methylenebis(4-alkyl-6-t-butylphenol) compounds such as 2,2'-methylenebis(4-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-400") and 2,2'-methylenebis(4-ethyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-500"); bisphenols such as 4,4'-butylidenebis(3-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage W-300"), 4,4'-methylenebis(2,6-di-t-butylphenol) (manufactured by the Laporte Performance Chemicals under the trade designation "Ionox 220AH"), 4,4'-bis(2,6-di-t-butylphenol), 2,2-(di-p-hydroxyphenyl)propane (Bisphenol A,), 2,2-bis(3,5-di-t-butyl-4-hydroxyphenyl)propane, 4,4'-cyclohexylidene-bis(2,6-di-t-butylphenol), hexamethylene glycol bis[3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L109"), triethylene glycol bis[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionate] (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Tominox 917"), 2,2'-thio[diethyl-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionate] (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L115"), 3,9-bis{1,1-dimethyl-2-[3-(3-t-butyl-4-hydroxy-5-methylphenyl)propionyloxy]-ethyl}2,4,8,10-tetraoxaspiro[5,5]undecane (manufactured by the Sumitomo Kagaku Co. under the trade designation "Sumilizer GA80"),

- 11 -

4,4'-thiobis(3-methyl-6-t-butylphenol) (manufactured by the Kawaguchi Kagaku Co. under the trade designation "Antage RC") and 2,2'-thiobis(4,6-di-t-butylresorcinol); polyphenols such as tetrakis[methylene-3-(3,5-di-t-butyl-4-hydroxyphenyl)propionato]methane (manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irganox L101"), 1,1,3-tris(2-methyl-4-hydroxy-5-t-butylphenyl)butane (manufactured by the Yoshitomi Seiyaku Co. under the trade designation "Yoshinox 930"), 1,3,5-trimethyl-2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl)benzene (manufactured by Ciba Speciality Chemicals under the trade designation "Irganox 1330"), bis[3,3'-bis(4'-hydroxy-3'-t-butylphenyl)butyric acid]glycol ester, 2-(3',5'-di-t-butyl-4-hydroxyphenyl)-methyl-4-(2",4"-di-t-butyl-3"-hydroxyphenyl)methyl-6-t-butylphenol and 2,6-bis(2'-hydroxy-3'-t-butyl-5'-methylbenzyl)-4-methylphenol; and phenol/aldehyde condensates such as the condensates of p-t-butylphenol and formaldehyde and the condensates of p-t-butylphenol and acetaldehyde.

Examples of phosphorus-based antioxidants include triaryl phosphites such as triphenyl phosphite and tricresyl phosphite, trialkyl phosphites such as trioctadecyl phosphite and tridecyl phosphite, and tridodecyl trithiophosphite.

These antioxidants can be used individually, or in the form of mixtures, conveniently in amounts within the range of from 0.01 to 2.0 parts by weight per 100 parts by weight of base oil.

The metal deactivating agents which can be used in the lubricating oil composition of the present invention include benzotriazole and the 4-alkylbenzotriazoles such as 4-methylbenzotriazole and 4-ethylbenzotriazole; 5-alkylbenzotriazoles such as 5-methylbenzotriazole, 5-ethylbenzotriazole; 1-alkylbenzotriazoles such as

- 12 -

1-dioctylaminomethyl-2,3-benzotriazole; benzotriazole derivatives such as the 1-alkyltolutriazoles, for example, 1-dioctylaminomethyl-2,3-tolutriazole; benzimidazole and benzimidazole derivatives such as the 5 2-(alkyldithio)-benzimidazoles, for example, 2-(octyldithio)-benzimidazole and 2-(decyldithio)benzimidazole and 2-(dodecyldithio)-benzimidazole; 2-(alkyldithio)-toluimidazoles such as 2-(octyldithio)-toluimidazole and 2-(decyldithio)-toluimidazole, 2-(dodecyldithio)-toluimidazole; indazole and indazole derivatives of toluimidazoles such as 10 4-alkylindazole and 5-alkylindazole; benzothiazole, 2-mercaptobenzothiazole derivatives (manufactured by the Chiyoda Kagaku Co. under the trade designation "Thiolite 15 B-3100") and 2-(alkyldithio)benzothiazoles such as 2-(hexyldithio)benzothiazole and 2-(octyldithio)benzothiazole; 2-(alkyl-dithio)toluthiazoles such as 20 2-(benzyldithio)toluthiazole, 2-(octyldithio)tolu-thiazole, 2-(N,N-dialkyldithiocarbamyl)benzothiazoles such as 2-(N,N-diethyldithiocarbamyl)benzothiazole, 2-(N,N-dibutyldithiocarbamyl)benzotriazole and 2-(N,N-dihexyldithiocarbamyl)benzotriazole; benzothiazole derivatives of 2-(N,N-dialkyldithiocarbamyl)toluthiazoles 25 such as 2-(N,N-diethyldithiocarbamyl)toluthiazole, 2-(N,N-dibutyldithiocarbamyl)toluthiazole, 2-(N,N-dihexyldithiocarbamyl)toluthiazole; 2-(alkyl-dithio)benzoxazoles such as 2-(octyldithio)benzoxazole, 2-(decyldithio)benzoxazole and 2-(dodecyldithio)-benzoxazole; benzoxazole derivatives of 2-(alkyldithio)-toluoxazoles such as 30 2-(octyldithio)toluoxazole and 2-(decyldithio)toluoxazole, 2-(dodecyldithio)toluoxazole; 2,5-bis(alkyldithio)-1,3,4-thiadiazoles such as 2,5-bis(heptyldithio)-1,3,4-thiadiazole, 2,5-bis(nonyldithio)-1,3,4-thiadiazole and 2,5- 35

- 13 -

5 bis(dodecyldithio)-1,3,4-thiadiazole, 2,5-bis-
 (octadecyldithio)-1,3,4-thiadiazole; 2,5-bis(N,N-
 dialkyldithiocarbamyl)-1,3,4-thiadiazoles such as 2,5-
 bis(N,N-diethyldithiocarbamyl)-1,3,4-thiadiazole, 2,5-
 bis(N,N-dibutyldithiocarbamyl)-1,3,4-thiadiazole and 2,5-
 bis(N,N-dioctyldithiocarbamyl)1,3,4-thiadiazole;
 thiadiazole derivatives of 2-N,N-dialkyldithiocarbamyl-5-
 mercapto-1,3,4-thiadiazoles such as 2-N,N-
 dibutyldithiocarbamyl-5-mercaptop-1,3,4-thiadiazole and 2-
10 N,N-dioctyldithiocarbamyl-5-mercaptop-1,3,4-thiadiazole,
 and triazole derivatives of 1-alkyl-2,4-triazoles such as
 1-dioctylaminomethyl-2,4-triazole.

15 These metal deactivating agents can be used
 individually or in the form of mixtures, conveniently in
 an amount within the range of from 0.005 to 0.5 parts by
 weight, preferably in the range of from 0.01 to 0.5 parts
 by weight, per 100 parts by weight of base oil.

20 The materials which can be used as anti-foaming
 agents include, for example, dimethylpolysiloxane,
 organosilicates such as diethylsilicate, the
 fluorosilicones, and non-silicone based anti-foaming
 agents such as poly(alkylene acrylate). These materials
 can be added and used individually, or in the form of
 mixtures, conveniently in an amount of from 0.0001 to 0.1
25 part by weight per 100 parts by weight, of base oil.

30 The viscosity index increasing agents which can be
 used include, for example, polymethacrylates and
 ethylene/propylene copolymers, other non-dispersion type
 viscosity index increasing agents such as olefin
 copolymers like styrene/diene copolymers, and dispersible
 type viscosity index increasing agents where a nitrogen
 containing monomer has been copolymerized in such
 materials. These materials can be added and used
 individually or in the form of mixtures, conveniently in

- 14 -

an amount within the range of from 0.05 to 20 parts by weight, per 100 parts by weight of base oil.

5 Examples of flow-point reducing agents include polymethacrylate based polymers. These materials can be added and conveniently used in an amount within the range from 0.01 to 5 parts by weight per 100 parts by weight of base oil.

10 Examples of the cleaning and dispersing agents which can be used include metal-based detergents such as the neutral and basic alkaline earth metal sulphonates, alkaline earth metal phenates and alkaline earth metal salicylates, alkenylsuccinimide and alkenylsuccinimide esters and their borohydrides, and ashless dispersing agents which have been modified with sulphur compounds. 15 These agents can be added and used individually, or in the form of mixtures, conveniently in an amount within the range of from 0.01 to 1 part by weight, per 100 parts by weight of base oil.

20 Examples of extreme pressure additives, anti-wear agents and friction controlling agents include sulphur based extreme pressure additives and anti-wear agents such as dialkyl sulphides, dibenzyl sulphide, dialkyl polysulphides, dibenzyl disulphides, alkyl mercaptans, dibenzothiophene and 2,2'-dithiobis(benzothiazole); 25 phosphorus based extreme pressure additives and anti-wear agents such as the acidic phosphate esters, trialkyl phosphates, triaryl phosphates and trialkyl phosphonates, trialkyl phosphites, triaryl phosphites and dialkylhydrozine phosphite, and phosphorus and sulphur based extreme pressure additives and anti-wear agents such as trialkyl trithiophosphites, triaryl phosphorothioates, dialkyl dithiophosphoric acid, 30 trialkyl dithiophosphate esters, acidic thiophosphate esters and zinc dialkyl dithiophosphates; aliphatic friction controlling agents such as fatty acid amides and 35

- 15 -

fatty acid esters, amine-based friction controlling agents such as the primary - tertiary alkylamines, and the alkylene oxide adducts of alkylamines, and extreme pressure additives and friction controlling agents such 5 as the zinc alkyldithiophosphates. These extreme pressure additives, anti-wear agents and friction controlling agents can be used individually, or in the form of mixtures, conveniently in an amount within the range from 0.05 to 5.0 parts by weight, and preferably 10 from 0.05 to 2 parts by weight, per 100 parts by weight of base oil.

The known anti-emulsification agents (which are used to break down emulsions and separate the emulsion into two layers) which are generally used as lubricating oil 15 additives can also be used. These agents include polyalkylene glycol based non-ionic surfactants, for example, polyoxyethylene alkyl ethers, polyoxyethylene alkylphenyl ethers and polyoxyethylene alkylnaphthyl ethers. These agents may be conveniently used in an 20 amount within the range of from 0.0005 to 0.5 part by weight, per 100 parts by weight of base oil.

The lubricating oil composition of the present invention is useful as a hydraulic oil composition, a compressor oil composition, a turbine oil composition, a 25 bearing oil composition and/or a gear oil composition.

The invention will now be described with reference to the following Examples which are not intended to limit (the scope of the present invention) in any way.

Examples

30 The present invention is described specifically below by means of hydraulic oil working Examples.

A hydrogenation refined base oil having a kinematic viscosity 31 mm²/s at 40°C, a viscosity index of 107, a sulphur content of less than 5 ppm, an aniline point of

- 16 -

112°C and a nitrogen content of less than 1 ppm, was used as the base oil for preparing sample oils.

5 β -dithiophosphonylpropionic acid, as indicated below in Table 1, was added to said base oil to yield the base lubricating oil composition.

10 The minimum amount of conventional anti-rust agent required in order that no rust formed in the anti-rust test was added to said base lubricating oil composition in Comparative Examples 2 to 6. In Comparative Example 7, less than the required amount of anti-rust agent was added to said base lubricating oil composition. In Comparative Example 1, no anti-rust agent was added to said base lubricating oil composition.

15 The minimum failure load for the sample oil in an FZG gear wheel test was used to investigate the effect of the anti-rust agents on the load resisting capacity. The results obtained are shown in Table 2.

20 The methods used for the various performance tests in the Examples and Comparative Examples are indicated below.

TABLE 1

BASE LUBRICATING OIL COMPOSITION	
Base Oil	99.980 %w
3-(o,o-diisobutyldithiophosphoryl)-2-methylpropionic acid	0.020 %w

Anti-rust Test

25 In order to evaluate the anti-rust performance of the sample oils, an anti-rust test was carried out for 24 hours at 60°C in the presence of artificial seawater in accordance with ASTM D665. It was investigated whether or not rust had formed on the steel specimen after the test.

- 17 -

FZG Gear Wheel Test

In order to evaluate the lubrication performance of the sample oils in gear wheel equipment, the A test gear wheels were used in accordance with ISO/WD14635-1 and the 5 gears were run for 15 minutes at each loading stage at an initial oil temperature of 90°C and a motor speed of 1450 rpm. The loading stage at which scorching occurred on the tooth surface of the test gear wheel as the load was being increased in stages was observed.

10

Example 1 and Comparative Examples 1 to 7

The compositions and test results are shown in Table 2.

TABLE 2

Example/Comparative Example	Example 1	Comp.Ex. 1	Comp.Ex. 2	Comp.Ex. 3	Comp.Ex. 4	Comp.Ex. 5	Comp.Ex. 6	Comp.Ex. 7
Base Lubricating Oil Composition, wt%	100	100	100	100	100	100	100	100
Conventional Polyalkylenesuccinic acid half ester (1)	-	-	0.05	-	-	-	-	-
Anti-rust Agent Component wt%								
N-Oleylsarcosinate (2)	-	-	-	0.04	-	-	-	-
Nonyl phenoxyacetate (3)	-	-	-	-	0.04	-	-	-
N-Acy1-N-alkoxyalkyl aspartic acid ester/imidazole derivative (4)	-	-	-	-	-	0.04	-	-
N-Acy1-N-alkoxyalkyl aspartic acid ester (5)	-	-	-	-	-	-	0.20	0.10
Anti-rust Agent (B) of the present Invention	Polyamide obtained from tetraethylene pentamine and acid (a mixture of stearic acid and isostearic acid in the proportions by weight of 80 : 20) (6)	0.05	-	-	-	-	-	-
Anti-rust Test Result	No Rust	Rust Formed	No Rust	Rust Formed				
FZG Gear Wheel Test Result Minimum Failure Load Stage	>12	>12	8	8	8	9	9	10

(NOTES)

- (1) manufactured by the Lubrizol Co. under the trade designation "Lubrizol 859"
- (2) manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Sarcosil O"
- (3) manufactured by the Ciba Speciality Chemicals Co. under the trade designation "Irgacore NPA"
- (4) manufactured by the Colonial Chemical Co. under the trade designation "Korakoa 93"
- (4) (CAS No. 68906-34-3, 27136-73-8)
- (5) manufactured by the King Industries Co. under the trade designation "KX1031"
- (5) Anti-rust agent disclosed in US-A-5,275,749
- (6) Amide bonded with 3.3 mol of a mixture of stearic acid and isostearic acid in proportions by weight of 80 : 20 per 1 mol of tetraethylenepentamine.

- 20 -

Rust formed during the anti-rust test in the case of the sample oil of Comparative Example 1 as no anti-rust agent was compounded therein. However, an excellent load resisting performance due to the β -dithiophosphoryl-propionic acid was confirmed in the FZG gear wheel test.

When a conventional anti-rust agent, as generally used in the art, was added to the base lubricating oil composition so as to pass the anti-rust test, in Comparative Examples 2 to 6, it was clear that this resulted in a marked reduction in the load resisting performance in the FZG gear wheel test. Consequently, it was necessary to increase the amount of the β -dithiophosphorylpropionic acid extreme pressure additive in order to obtain a higher level of load resisting performance.

In contrast, when a polyalkylenopolyamide (B) of the present invention was added as the anti-rust agent in Example 1, there was virtually no lowering of the load resisting performance due to the β -dithiophosphoryl-propionic acid and the sample also passed the anti-rust test. Thus, the amount of β -dithiophosphorylpropionic acid added to such a sample oil could be minimised.

Example 2

Example 1 was repeated except that the polyamide (7) obtained by amide bonding 3.3 mol of acid (a mixture of stearic acid and isostearic acid in the proportions by weight of 50 : 50) with 1 mol of tetraethylenepentamine was used instead of the polyamide (6) obtained with a mixture of stearic acid and isostearic acid in the proportions by weight of 80 : 20 with tetraethylenepentamine as used in Example 1.

The results obtained indicated that there was no rust formation in the anti-rust test, whilst the result

- 21 -

in the FZG gear wheel test (minimum failure loading stage) was >12.

Example 3

5 Example 1 was repeated except that the polyamide (8) obtained by amide bonding 3.3 mol of oleic acid with 1 mol of tetraethylenepentamine was used instead of the polyamide (6) obtained with a mixture of stearic acid and isostearic acid in the proportions by weight of 80 : 20 with tetraethylenepentamine as used in Example 1.

10 The results obtained indicated that there was no rust formation in the anti-rust test, whilst the result in the FZG gear wheel test (minimum failure loading stage) was >12.

15 The lubricating oil compositions of the present invention are virtually free, or completely free, of metals which are harmful in respect of both the environment and safety and they have excellent anti-rust performance and load resisting performance in order to match the increased speeds, higher pressures and more 20 compact nature of modern industrial machinery.

C L A I M S

1. Lubricating oil composition, comprising a β -dithiophosphorylpropionic acid (A), a polyalkylenepolyamide (B) and base oil.
2. Lubricating oil composition according to Claim 1,
5 wherein the β -dithiophosphorylpropionic acid (A) is represented by the general formula (1) below:-
$$S=P(-O-R^1)_2SCH_2CH(R^2)COOH \quad (1)$$
wherein R¹, which may be identical or different, represents a branched alkyl group of from 3 to 8 carbon atoms, and R² represents a hydrogen atom or a linear or branched alkyl group of from 1 to 4 carbon atoms.
- 10 3. Lubricating oil composition according to Claim 2, wherein R² is hydrogen or a methyl group.
4. Lubricating oil composition according to any one of
15 Claims 1 to 3, wherein the β -dithiophosphorylpropionic acid (A) is selected from 3-(O,O-diisopropylidithiophosphoryl)propionic acid, 3-(O,O-diisopropylidithiophosphoryl)-2-methylpropionic acid, 3-(O,O-diisobutyldithiophosphoryl)propionic acid and 3-(O,O-diisobutyldithiophosphoryl)-2-methylpropionic acid.
- 20 5. Lubricating oil composition according to any one of Claims 1 to 4, wherein the β -dithiophosphorylpropionic acid (A) is present in amount of from 0.001 to 0.5 part by weight, per 100 parts by weight of base oil.
- 25 6. Lubricating oil composition according to any one of Claims 1 to 5, wherein the polyalkylenepolyamide (B) is obtained by reacting,
 - (i) a polyalkylenepolyamine represented by the general formula (2) below:-

- 23 -

wherein R^3 represents an alkylene group of from 2 to 4 carbon atoms, and M is an integer of value from 2 to 6, with

5 (ii) at least one type of carboxylic acid selected from the group comprising saturated monocarboxylic acids having from 12 to 30 carbon atoms and unsaturated monocarboxylic acids having from 18 to 24 carbon atoms.

7. Lubricating oil composition according to Claim 6, wherein the carboxylic acid is a mixture of aliphatic 10 monocarboxylic acids selected from among the group comprising mixtures of aliphatic monocarboxylic acids of which the aliphatic group is a linear chain saturated alkyl group which has from 12 to 30 carbon atoms and aliphatic monocarboxylic acids of which the aliphatic 15 group is a branched saturated alkyl group which has from 12 to 30 carbon atoms, and mixtures of aliphatic monocarboxylic acids of which the aliphatic group is a linear chain unsaturated alkyl group which has from 18 to 24 carbon atoms and aliphatic monocarboxylic acids of which the aliphatic 20 group is a branched saturated alkyl group which has from 12 to 30 carbon atoms.

25 8. Lubricating oil composition, according to any one of Claims 1 to 7, wherein the polyalkylenopolyamide (B) is present in an amount of from 0.005 to 1 part by weight, per 100 parts by weight of base oil.

9. Lubricating oil composition according to any one of 30 Claims 1 to 8, wherein the base oil is a petroleum-based oil and/or a synthetic hydrocarbon-based oil with a kinematic viscosity of from 2 to 680 mm^2/s (40 °C), a total sulphur content of from 0 to 1 wt%, a total nitrogen content of from 0 to 100 ppm, and/or an aniline point of from 80 to 130 °C.

- 24 -

10. Lubricating oil composition according to any of
Claims 1 to 9, which is used as a hydraulic oil
composition, a compressor oil composition, a turbine oil
composition, a bearing oil composition and/or a gear oil
composition.

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